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On the polytypic phase transition 12R→2H in lead iodide

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ABSTRACT

Lead iodide has number of applications and is considered to be a potential room temperature radiation detector. The phenomenon of polytypism in PbI_2 *is posing a problem. Even when the* PbI_2 *crystals are stored for some time, there are structural changes in the crystals. It causes deterioration in functioning of devices. Considering a vast amount of data available on* PbI_2*, a comparative study on the growth and storage of* PbI_2 *crystals has been made and it has been concluded that impurities are responsible for the phase transformations. Further, it is suggested that the role played by vacancies can not be ignored.*

Key words: lead iodide, polytypism, impurities, phase transformations, Inorganic crystal structure.

INTRODUCTION

In the last few years, a lot of work has been done on the technology of radiation detectors. Lead iodide is one of the promising materials for room temperature radiation detector. Using PbI_2 as radiation detector do not require liquid nitrogen for cooling. People have been trying to grow pure PbI_2 crystals as it should have very low conductivity for the purpose of radiation detector [1]. Though HgI_2 is also a leading member having similar properties but lead iodide has an edge over HgI_2 because growing crystals of PbI_2 is simpler as compared to HgI_2 as lead iodide has lower vapor pressure than HgI_2 and better chemical stability. In addition to it, phase transition between orthorhombic and tetragonal phases of mercury iodide at 400K limits the bulk growth of HgI_2 and it can be grown by vapor phase only.

To obtain the pure material of lead iodide, the problem of polytypism (coalescence of different structures in a crystal, phase transformations due to native impurities and defects) causes deterioration of the performance of devices. Such effects have also been observed in polytypic Silicon Carbide [2]. For the fabrication of devices from PbI_2 crystals, a number of parameters are required to be controlled as per requirement therefore, initially it becomes necessary to grow the pure crystals of one's choice (free of polytypism) having reproducible properties.

Recently Matuchova et al. [3] studied the lead iodide crystals for their conductivity. Pure crystals have conductivity of the order $10^{-13}\ \Omega^{-1}cm^{-1}$. Further, a decrease in conductivity has been observed when crystals were doped with Ho and Tm but no satisfactory explanation has been given.

Considering a vast amount of data available on the PbI_2 structures grown by various methods by various researchers, a review has been made on the mode of growth of lead iodide crystals and phase transition in them when stored for few months. A deep understanding of phase transitions can be helpful in optimizing the method and conditions of growth of desired crystals for the fabrication of the devices from lead iodide.

MATERIALS AND METHODS

2. Basic structure of PbI_2

The PbI_2 structure consists of various stackings of PbI_2 sandwiches in each of which a layer of Pb ions is sandwiched between two close packed layers of iodine ions. I-Pb-I sandwich being the repeat unit and each Pb atom is surrounded by 6 I atoms forming a near octahedral $[PbI_6]^{4-}$. The interlayer interactions are more covalent than ionic and the electron density between the sandwiches is very low that results in weak van der-Walls interactions between the sandwiches [4] of the type

$U(R) = - d/R^6 + be^{-aR}$

R is the separation between the atoms.
a , b and d are constant characteristics of atoms.

In the case of PbI_2, the relative bond strengths between iodine atoms within a sandwich and iodine atoms between adjacent sandwich have been estimated around 80 [4] .This results in many polytypes and complicated phase changes amongst different polytypes. As I-Pb-I sandwich contains three layers of atoms and charge career dynamics perpendicular to these layers have several quantum states. This is in contrast to the two dimensional graphene where charge carrier dynamics involving direction perpendicular to the layers of carbon atoms can be pinned to the ground state.

3. Studies on the storage of lead iodide crystals

The data on structures of PbI_2 crystals grown by various methods and storage is presented in Tables 1, 2 and 3.

Table 1. Results of X-ray characterization of vapor grown PbI_2 crystals before and after storage

No. of crystals	Starting structure	Resulting structure
Jain & Trigunayat (1996)		
undoped crystals (20) 40 X-ray photographs	All 12R (40)	No change after storage
AgI doped crystals (20) 40 X-ray photographs	12R (13) (4H+12R) (16) (2H+12R) (11)	All crystals transform to 2H
Minagawa (1975)		
3	Ordered 12R (one with weak 4H)	2H (Even 4H→2H)
1	Ordered 12R	No change

The duration of storage time of crystals in all the cases is few months.

As shown in Table 1, the results of Jain &Trigunayat(1996)[9] show that in the case of vapor grown crystals, all the undoped crystals with structure 12R did not change after storage. But all the AgI doped crystals containing structures 12R,4H and 2H transform to 2H.The Minagawa (1975)[7] results also show the transformation 12R→2H after storage. They have not mentioned the purity of the material. From the results it is clear that impurities are playing a major role in phase transformations in vapor grown crystals.

Table 2. Results of X-ray characterization of gel grown PbI_2 crystals before and after storage

No. of crystals	Starting structure	Resulting structure
Soudmand & Trigunayat (1989)		
undoped crystals (20) 40 X-ray photographs	All 2H (40)	After heating converted to 12R but restored to 2H after storage
AgI doped crystals (15) 30 X-ray photographs	2H (21), 4H(3), 12H(2), 16H (1), 12R(3)	After heating converted to 12R but restored to 2H after storage.Higher polytypes 4H, 12H and 16H do not change to 2H
Minagawa (1975)		
4	Faulted 12R+weak 2H	Faulted weak 12R+intense 2H
2	Faulted 12R+weak 2H	No change
2	12R	Effect not mentioned
Salje et al (1987)		
1	12R+2H	2H
1	12R	12R
Minagawa (1981)		
5	Faulted 12R +weak 2H	Faulted weak12R + intense 2H

In the case of gel grown crystals (Table 2), it is observed that in all the cases crystals have tendency to retain the 2H structure even the 2H crystals got converted to 12R on heating but restored to 2H after storage. However, few AgI doped crystals containing higher polytypes reported by Soudmand & Trigunayat (1989) [5] having structure 4H, 12H and 16H did not change on heating or storage. In addition to it, Minagawa (1981)[6] have reported that 5 crystals with polytypes faulted 12R+ weak 2H got converted to weak faulted 12R+ intense 2H when stored. Similar results have been presented by Minagawa (1975) [7] and Salje et al. (1987) [8].

Table 3. Results of X-ray characterization of melt grown PbI_2 crystals before and after storage.

Chaudhary & Trigunayat (1987)		
Very pure crystals, 39 X-ray photographs (20 zone passes)	All 12R (39)	No change after storage
More pure crystals, 46 X-ray photographs (12-14 zone passes)	12R (36) (4H+12R) (8) (2H+12R) (2)	All transform to 2H except one
Less pure crystals, 75 X-ray photographs (6-8 zone passes)	12R (51) (12R+4H) (24)	No change after storage

Table 3 shows the results of storage for the crystals grown from melt by Chaudhary & Trigunayat (1987) [10]. No structural changes have been observed in very pure crystals and less pure crystals on storage. But in the case of crystals with intermediate level of impurity (12-14 zone passes) all (containing structures 4H and 12R) crystals got transformed to 2H exept one.

DISCUSSION

The observed admixture of 4H and 12R in a number of crystals shows that 4H represents a favorable metastable phase of lead iodide. The unit cell of 12R consists of 3 units of 4H rotated through 60^o in succession (The Zhdanov sequence of 4H and 12R being ABCB/ABCB/ABCB/….. and ABCB/CABA/BCAC/…..respectively).

Such observation on storage has also been made by Trigunayat in similar polytypic CdI_2 crystals [11]. When solution grown crystals of CdI_2 were stored for three to four years at room temperature, all the crystals got transformed to other structures.

From above studies it is clear that
1. In gel grown crystals impurities are responsible for creation of few higher polytypes.
2. In the case of AgI doped vapor grown crystals and the crystals grown from melt with intermediate impurities, all the structures got transformed to 2H.
3. Phase transition 2H→12R is governed by temperature whereas 12R→ 2H is governed by impurities/ time effect.

It would be interesting to cool the 12R crystals to a low temperature and observe for a fast 12R→ 2H transformation.

In short, impurities play a role in phase transitions in all the methods of crystal growth specifically when crystals are grown at high temperatures. From the data and other studies made, it is concluded that removal of impurities (purification) and addition of known desired amount of impurities (doping) can help to grow a required stable structure of one's choice that may not transform with passage of time.

In all the above studies there is no discussion of vacancies. It is expected that an atom surrounded by vacancies is more mobile than others. In a theoretical study, Ito et al. [12] have calculated that in the case of SiC with Si vacancy, 6H structure is formed and in the case of C vacancy 4H structure is favored. It shows that vacancies in SiC play an important role in stabilizing a particular structure. Some experimental work is also being done on the PbI_2 crystals [13].

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